RJOAS: Russian Journal of Agricultural and Socio-Economic Sciences
ISSN 2226-1184 (Online) | Issue 4(148), April 2024

UDC 631

DYE SENSITIZED SOLAR CELL (DSSC) PERFORMANCE WITH DRIED DYE OF EICHHORNIA CRASSIPES LEAVES AS PHOTOSENSITIZER

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ABSTRACT
DSSC is solar based electrical energy with dye organic matter as sensitizer. The organic sensitizer used to be a freshly extracted pigment. This study used organic dye that had previously been prepared in dry form. This dry dye is more practical to be used in DSSC without taking a long time for extraction. The organic dye derived from Eichhornia crassipes (water hyacinth) leaves. The leave's extract was dried by using a foam mat drying method with the fillers of dextrin (10% w/v) and gum Arabic (10% w/v), and egg white (2% w/v) as a foaming agent. The application of dried dye was arranged in 2, 4, 6, 8 and 10% (w/v, ethanol solvent), and a freshly prepared extract was also performed as a control. The results showed that the highest amount (0.63 mg/L) of chlorophyll content was in DSSC with the application of 10% (w/v) dried dye. The best DSSC electrical performance was found in the treatment of 4% dried dye with the electrical characteristics including: Voc: 589 mV, Isc: 0.0408 mA, Vmax: 230 mV, Imax: 0.0347, fill factor: 0.332, Output: 7.98 mW and efficiency: 4.95%.

KEY WORDS
DSSC, eichhornia crassipes, dried dye, photosensitizer.

Natural DSSC is a photoelectrochemical device that converts sunlight energy in the form of photons into electrical energy by utilizing an organic layer (dye) as a photosensitizer. The DSSC includes a transparent conductor oxide layer, a photosensitizer, an electrolyte solution and a counter electrode (Erande et al., 2020). DSSC has attracted a lot of attention due to several advantages including: simple fabrication with low cost, structural compatibility, and high photoelectric conversion efficiency (Zanjanchi & Beheshtian, 2019). The natural photosensitizer in the DSSC structure has an important role in the redox cycle. Photosensitization is a process of light harvesting and electron injection carried out by dye from low energy levels to the conduction band of the semiconductor. This shows that the dye layer is a determinant of the performance of DSSC (Halidun et al., 2018).

There has been many research conducted on natural pigments due to several advantages of natural dyes compared to synthetic dyes, including natural dye are not toxic and low fabrication costs. In addition, some previous workers reported a fairly good efficiency (Juhász Junger et al., 2019). One of the potential resources in low land of South Sumatra is water hyacinth (*Eichhornia crassipes*). This plant is a type of weed that has the potential as a source of chlorophyll.

Water hyacinth, especially the leaves, contain relatively higher amount of chlorophyll when compared to other compounds such as flavonoids, amino acids, fibre or cellulose, as well as components of organic matter and cyanide (Hasibuan et al., 2020). Dye for photosensitizer is obtained through the process of material extraction by cold extraction by using sonication method. This modern extraction has been carried out with the aim of obtaining more extract yields. Dye photosensitizers are generally directly applied to the DSSC as a layer of the working electrode in the liquid phase after being obtained from the extraction. The weakness of the liquid phase in its use as a dye sensitizer, among others: pigments are easily degraded so that the quality of the dye decreases and the storage period cannot last long.

The next development of innovation in the use of dye photosensitisers is to convert the liquid phase dye into a solid phase (powder) so that it has a longer shelf life. The extracted dye is then dried so that it can be stored for further fabrication. One of the simple drying methods that can be used to preserve natural dye is foam mat drying method. This drying method utilizes a foaming agent and filler as a binding medium for the extract. The drying temperature ranges from 40 to 80^{o}C. The dried solids are scraped from the pan and then sifted to get powdered dye (Izadi et al., 2020).

The foam that forms a layer in the drying process causes the material to evaporate faster so that drying can take place in a shorter time. The reason is that the liquid will move faster in the foam layer than through the solid layer. The surface area will increase as the foam concentration increases and form a porous structure in the material that allows heating of the entire surface. This makes the drying process (evaporation of water) faster (Mounir, 2017). Foam layer drying method has a low dissolution time and hygroscopicity which has an impact on the quality of the powder material and shelf life (El-Salam et al., 2021)

The performance of DSSC is generally influenced by dye, so the addition of dye concentration will increase the resulting performance. Dye with a certain concentration will have an effect on the increase in the amount of dye attached to the TiO_2 pore layer or semiconductor, so that more electrons are excited and form a redox cycle and improve DSSC performance. According to (Arifin et al., 2017), on the effect of liquid dye with different concentrations on the performance of DSSC using chlorophyll extract from papaya leaves and through treatment with concentrations of 60%, 70%, 80%, 90% and 100%, indicating that the best treatment lies at a concentration of 90%. The dye with a concentration of 100% decreased due to the accumulation of dye on the TiO_2 semiconductor layer. The build-up of dye will increase the inactive dye and block the electron injection process into the TiO_2 semiconductor layer, to carry out the redox cycle.

Based on the previous work, this research work on the dried dye for photosensitizer of water hyacinth leaves by using cold extraction of sonication. The extracted dye was further dried through a method of foam mat drying. The dried dye is then applied as photosensitizer for DSSC. Its electrical performance was then evaluated in various concentrations of dried dyes.

METHODS OF RESEARCH

The natural dye was extracted from water hyacinth leaves. The leaves were thoroughly washed with water and weighed as amount of 100 g. The leaves were crushed in a blender for 3 minutes at a medium speed in the ratio of water and water hyacinth leaves 2:1. The crushed leaves were further extracted by using the ultrasonic assisted extraction method for 45 minutes at a temperature of 35^{o}C. The leaf pulp was filtered through a filter paper. An amount of 25 mL of the filtrate was used for the control treatment (fresh extract) (C-treatment). The dried dye was processed by a method of foam mat drying. The foaming agent used was egg white 2% (w/v). There were two kinds of fillers (dextrin and gum Arabic) were used prior to be dried by a foam mat drying method at 60^{o}C. Each filler was added as amount of 10% (w/v). A-treatment denoted for the filler of gum Arabic, and B-treatment for dextrin. The dried dye was sifted through an 80-mesh sieve. Each dried dye was applied on the DSSC at the concentrations of 2, 4, 6, 8 and 10% (w/v) in ethanol.

TiO_2 powder was ground using a mortar and sieved through a 100mesh sieve. It was weighed as much as 6 g and put into a 25 mL Beaker glass and 0.1 N acetic acid solution was added to it and stirred until evenly mixed. Then 10 drops of TritonX-100 solution were added and stirred evenly. This TiO_2 paste is ready to be smeared on the conductive glass.

Potassium iodide (0.5 M) as much as 0.8 g was added to 10 mL of distilled water and stirred until evenly distributed. Five drops of iodine were dropped into the solution and stirred for 10 minutes using a magnetic stirrer. This electrolyte solution is ready to use.

Conductive glass is coated with carbon by covering the glass layer using carbon from burning candle until the entire surface of the glass was evenly covered by carbon.

The conductive glass has a rectangular shape with a size of 25 mm × 25 mm × 1.1 mm which has been coated with Indium Tin Oxide (ITO) was used. The conductive glass that was given a barrier is then smeared with TiO_2 paste evenly with a thickness according to the thickness of the scotch tape. The conductive glass was allowed to stand for 30 minutes and then burned in a muffle furnace at 350°C for 15 minutes. The conductive glass was left to cool down at room temperature and then it was immersed in dye. Dye was absorbed by TiO_2 during immersion. The conductive glass was dried on a hot plate at 100°C for 2 minutes. The conductive glass that had absorbed dye and a conductive glass with carbon was then combined and clamped with paper clips. The electrolyte solution that has been prepared was then dripped between two conductive glasses.

The measured parameters included: dye absorbance and DSSC performance (current and voltage) measured by using a multimeter that had been connected to a series of measurement device. The chlorophyll content in water hyacinth leaves was calculated using the calculation formula for the Wintermans and De Mots method as in Posumah's research (Posumah, 2017) according to Equations (1) and (2).

Chlorophyll a= (13.7 x A665) – (5.76 x A649) (1)

Chlorophyll b= (25.8 x A649) – (7.60 x A665) (2)

Total chlorophyll content was calculated according to Equation (3):

Chlorophyll Total= (20.0 x A649) + (6.10 x A665) (3)

The electrical performance using a simulation device whose light source uses a Solar Simulator. The observed parameter was V_{oc}, I_{sc}, FF as well as current, voltage, efficiency (η) and stability.

$$FF = \frac{V_{max} \times I_{max}}{V_{oc} \times I_{oc}} \quad (4)$$

$$\eta\,(\%) = \frac{P_{max}}{P_{in}} \times 100\% \quad (5)$$

RESULTS AND DISCUSSION

Absorbance measurements were carried out using a UV-Vis 752 spectrophotometer. The measurement results as depicted in Figure 1. Absorbance is a quantity that indicates the ability of a material to absorb light. Organic compounds are able to absorb light because their valence electrons can be excited to a higher energy level (Ridwan et al., 2018). Based on the maximum wavelength peak shown in Figure 1, there was chlorophyll in the extracted dye.

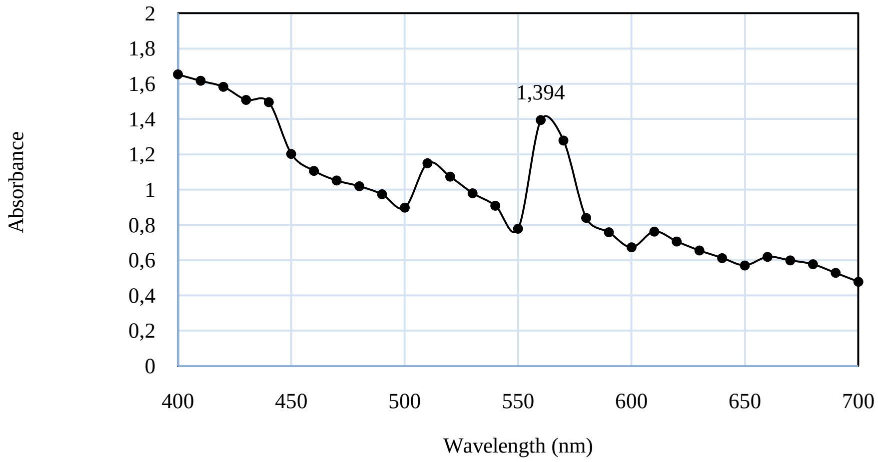

Figure 1 – Absorption spectra of dye

The chlorophyll content of each photosensitizer as shown in Figure 2. It showed an increase in chlorophyll content along with the increasing of dye concentration. The samples which were dried using the foam mat drying method with filler of gum Arabic showed a higher yield than using dextrin. The highest chlorophyll content (14.62 mg/L) was found in 10% addition of dye photosensitizer with gum Arabic as a filler.

Absorbance is a quantity that indicates the ability of a material to absorb light. Organic compounds are able to absorb light because their valence electrons can be excited to a higher energy level (Ridwan et al., 2018). Based on the maximum wavelength peak in Figure 1 showed that there was chlorophyll in the extracted dye. (Semalti & Sharma, 2020) stated that pigments significantly converted light into electricity depending on the band gap of the photovoltaic system. The ability of pigments to convert light into electricity must meet several criteria, including: absorbance in the visible light spectrum area, intense adsorption of pigment particles on the semiconductor surface and the presence of electron excitation in the dye which is then injected into the conduction band. semiconductor (TiO_2 layer).

Photoexcitation in DSSC did not occur at the semiconductor electrode but occurs at the light-absorbing pigment or at the interface between the color-sensitive semiconductor and the electrolyte. Electron injection from dye to TiO_2 required pigment excitation which was more reductive than TiO_2 conduction band. The electrons in the conduction band of the semiconductor were collected in a counter electrode which flowed through an external circuit. The oxidized dye then accepted electron donors from the electrolyte solution to bring it back to its initial state. The mechanism continued to repeat which was referred to as photo electrochemistry (Ridwan et al., 2018). Chlorophyll has many conjugated double bonds with the ability to absorb visible light. However, all types of chlorophyll have certain absorption wavelengths due to differences in structure. Chlorophyll molecules absorb blue and red wavelengths, as shown by the peaks in the absorption spectra in Figure 1.

Chlorophyll absorbs light and gets its green color by reflecting green wavelengths. This function is to involve the accumulation of sunlight, transfer solar energy into chemical energy and transfer electrons (Semalti & Sharma, 2020). Chlorophyll which functions as a light energy harvester tends to absorb red and blue light. Chlorophyll can be divided into several types including a, b, c, d and e, besides that there is also chlorophyll f which has been identified in recent years.

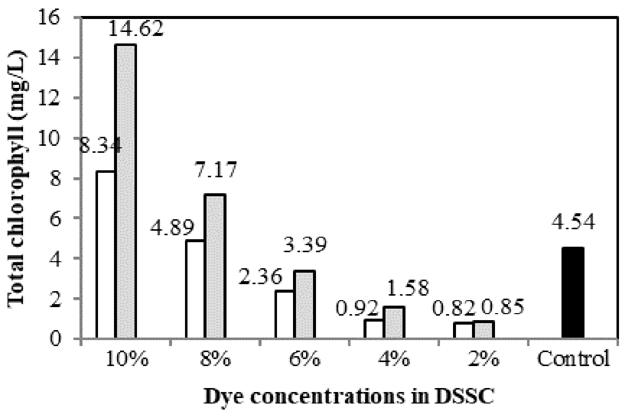

Figure 2 – Total chlorophyll in dye

Figure 2 showed an increase in chlorophyll content along with the increasing of dye concentration. The samples which were dried using the foam mat drying method with filler of gum Arabic showed a higher yield than using dextrin. The highest chlorophyll content (14.62 mg/L) was found in 10% addition of dye photosensitizer with gum Arabic as a filler. Gum Arabic was a natural response (sap) when an injury occurred on the bark of the Acacia Senegal tree. Gum Arabic is soluble in water but insoluble in alcohol. Gum Arabic has a composition of water content 11 to 15%, protein content 2 to 2.4%, lipid 0.1 to 0.6%, hygroscopicity 26 to 40% and swelling index 1.56 to 4.00 (Rosland Abel et al., 2020)

Gum Arabic is a series of units of D-galactose, L-arabinose, L-rhamnose and D-galacturonic acid that can increase the total dissolved solids. This was in accordance with the findings showing that as the dye concentration increases, the pigment content also increased. Gum Arabic also has the ability to bind water and can thicken materials so that apart from producing more solids, gum Arabic also increased the plasticity of material and has a better texture (Ketaren et al., 2017). This is in line with research results which generally showed that the quantity of chlorophyll content was higher using gum Arabic as a filler than dye using dextrin as a filler.

The characteristics of I-V DSSC with various concentrations of dry dyes as presented in Table 1. The curve of current and voltage with the fillers of dextrin and gum Arabic as well as dye with no filler were depicted in Figure 3 to Figure 5.

Table 1 – The characteristics of I-V DSSC with various concentrations of dried dyes

Dried-Dye	V_{oc} (mV)	I_{sc} (mA)	V_{max} (mV)	I_{max} (mA)	FF	P_{output} (mW)	Efficiency (%)
B; 2%	787	0.0185	312	0.0107	0.229	3.34	2.12
A; 2%	701	0.0167	423	0.0098	0.354	4.15	2.61
B; 4%	589	0.0408	230	0.0347	0.332	7.98	4.95
A; 4%	746	0.0312	298	0.0202	0.259	6.02	3.77
B; 6%	767	0.0236	501	0.0134	0.371	6.71	4.25
A;6%	663	0.0201	356	0.0135	0.361	4.81	3.03
B; 8%	430	0.0053	313	0.0020	0.275	0.63	0.40
A; 8%	638	0.0255	294	0.0161	0.291	4.73	2.89
B; 10%	250	0.0042	135	0.0019	0.244	0.26	0.16
B; 10%	486	0.0040	230	0.0023	0.272	0.53	0.33
Control	680	0.0478	362	0.0338	0.376	12.24	7.58

Note: A=gum Arabic; B=dextrin; C=control.

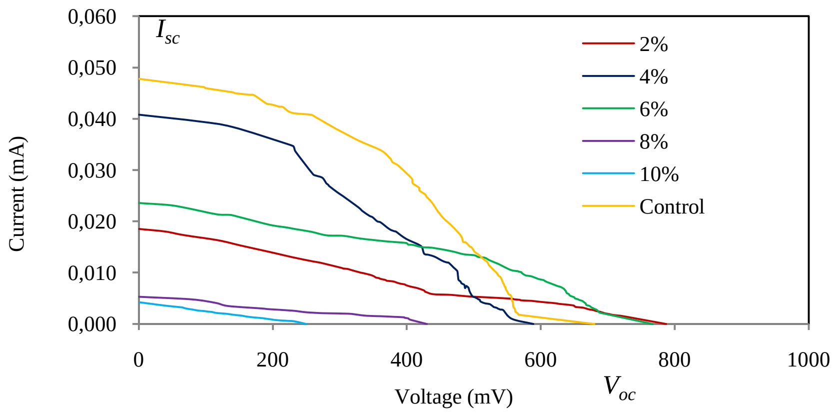

Figure 3 – I-V Curve with dextrin as filler in dye

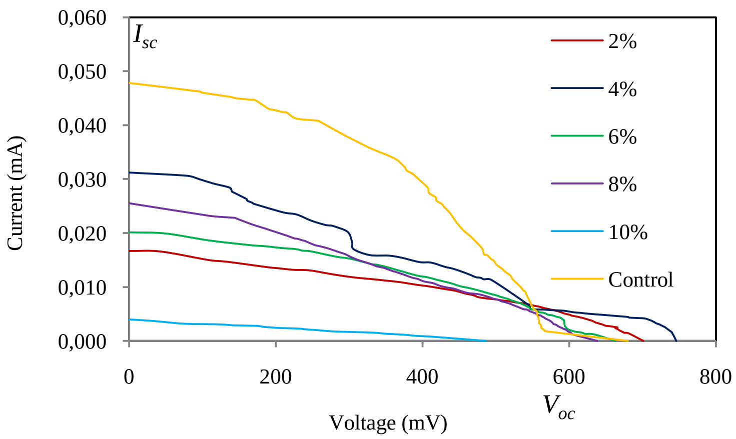

Figure 4 – I-V Curve with Arabic gum as filler in dye

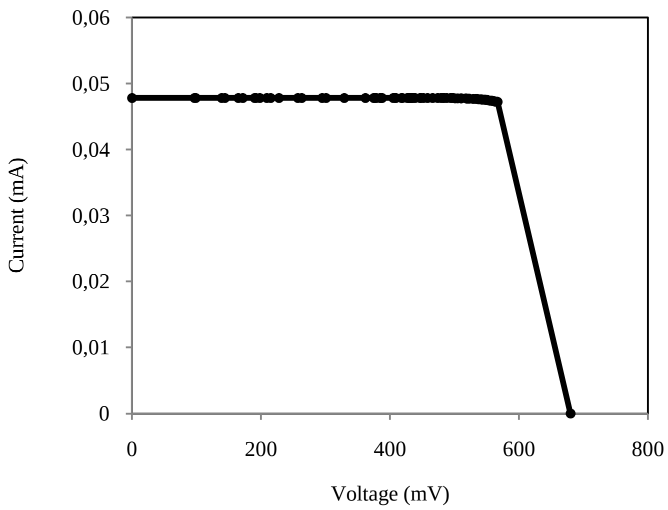

Figure 5 – I-V Curve with control-dye (no filler)

Measurement of voltage and current using a series of voltmeters and ammeters with an average light intensity sourced from halogen lamps of 327.56 W/m^2. Electrolyte solution added to the DSSC component was carried out prior to the measurement which was as an electron provider. It functioned as an electron donor in the dye whose electrons have been excited. The value of voltage and current are inversely proportional during the measurement process, it was due to the increasing temperature had an impact on decreasing voltage. The current would increase along with the increase in temperature originating from the light source (Richhariya et al., 2017).

The current and voltage data obtained were then used to calculate and determine the value of several DSSC performance parameters such as recharging factor (ratio of actual power between maximum voltage and maximum current), maximum power and efficiency. The mechanism occurred in DSSC was indirectly similar to photosynthesis. Dye replaced chlorophyll as a light-harvesting element to produce electrons to be excited. Carbon dioxide in the photosynthesis process was replaced by a TiO_2 layer in the DSSC cycle, then electrolyte replaced water and the multilayer structure aimed to increase light absorption and electron collection efficiency (Adedokun et al., 2016)

Based on the I-V curves as shown in those Figures, the control-dye in DSSC gave a straight line between the voltage of 0 to 600mV that indicated control-dye had a better stability in DSSC than other dyes. The current and voltage curves also showed that DSSC with dried dye gave a fair stability at the concentration of 4% dried-dye for both fillers of dextrin and gum Arabic.

The best performance of DSSC was found in the control dye with an efficiency of 7.58%. The chlorophyll content in the dried-dye with dextrin and gum Arabic as a filler at a concentration of 2 to 4% was lower than the control dye, which was only 0.81 mg/l to 1.57 mg/L, but it was able to produce a fairly good performance. It showed that the dye fabrication using the foam mat drying method using dextrin and gum Arabic as a filler has a good effect on the performance of DSSC. However, the efficiency at increasing concentrations of 6%, 8% and 10% decreased sequentially, both in dried-dyes with dextrin and gum Arabic as fillers. Based on this, chlorophyll content affects the performance of DSSC. The performance of DSSC was getting better as the chlorophyll content in the dye increased, but at a certain concentration, the excess chlorophyll content causes the performance to decrease. This was caused by the accumulation of dye deposited on the TiO_2 layer. The accumulation of color-pigments could increase inactive color molecules and then inhibit the electron injection process in the oxidation-reduction cycle. This could be seen in DSSC at the concentration of 10% (w/v) with the highest total chlorophyll content of 14.6 mg/l but has the lowest efficiency of 0.33%. It can be concluded that the more stable the measurement process and the greater values of voltage and current resulted in a better efficiency.

DSSC fabrication using dried-dye obtained through foam mat drying method with dextrin and gum Arabic as filler had been successfully gave a good performance at the concentration of 4% dried-dye in DSSC that was indicated by the efficiency of 4.95% and 3.77%, respectively for the filler of dextrin and gum Arabic.

CONCLUSION

DSSC fabrication using dried-dye obtained through foam mat drying method with dextrin and gum Arabic as filler had been successfully gave a good performance at the concentration of 4% dried-dye in DSSC that was indicated by the efficiency of 4.95% and 3.77%, respectively for the filler of dextrin and gum Arabic.

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